Drivers of increasing iron concentrations in freshwaters

Björnerås, Caroline

2019

Document Version:
Publisher's PDF, also known as Version of record

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I. Björnerås, C., Weyhenmeyer, G. A., Evans, C. D., Gessner, M. O., Grossart, H. -P., Kangur, K., Kokorite, I., Kortelainen, P., Laudon, H., Lehtoranta, J., Lottig, N., Monteith, D. T., Nõges, P., Nõges, T., Oulehle, F., Riise, G., Rusak, J. A., Räike, A., Sire, J., Sterling, S., and Kritzberg, E. S. 2017. Widespread Increases in Iron Concentration in European and North American Freshwaters. Global Biogeochemical Cycles 31:1488-1500.

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Printed by Media-Tryck, Lund 2019 NORDIC SWAN ECOLABEL 3041 0903

LUND UNIVERSITY

ISBN: 978-91-7895-336-3

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Lund University

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Drivers of increasing iron concentrations in freshwaters

Caroline Björnerås

LUND
UNIVERSITY

DOCTORAL DISSERTATION

by due permission of the Faculty of Science, Lund University, Sweden.
To be defended at the Blue Hall, Ecology Building, Sölvegatan 31, Lund, Sweden
on the 29th of November at 9:30.

Faculty opponent
Roxanne Maranger

Université de Montréal, Canada

Organization LUND UNIVERSITY	Document name: Doctoral Dissertation
Department of Biology Sölvegatan 37, 22362 Lund, Sweden	Date of issue: 29th of November 2019
Author: Caroline Björnerås	Sponsoring organization

Title and subtitle: Drivers of increasing iron concentrations in freshwaters

Abstract

Iron (Fe) concentrations are increasing in freshwaters (lakes and streams) in Sweden, as well as in other regions in northern Europe. Together with increasing concentrations of organic matter, Fe is contributing to the ongoing browning of freshwaters, which may have serious ecological consequences and implications for ecosystem services.

The aim of this thesis was to investigated where, to what extent, and - primarily - *why* Fe concentrations are increasing in freshwaters.

As catchment soils are the main source of Fe in freshwaters, higher catchment influx could explain increases in Fe concentrations, but the positive trends could also be the result of changes in processes controlling the distribution of Fe within freshwater systems. I investigated how both of these processes are affected by changes in climate, atmospheric sulfate deposition, and land-use. These three potential drivers were hypothesized to affect pH, redox conditions and OM availability, factors controlling Fe speciation and thus Fe mobility in the landscape.

Analyses of temporal and spatial patterns in Fe concentrations from monitoring data of wide geographic distribution confirmed that positive Fe trends are widespread, and possibly more frequent in Northern Europe than in North America. Positive Fe trends were also more frequent in catchments with a high percentage of coniferous forest, and found in regions were precipitation had increased. Coniferous forest soils are particularly important sources of Fe due to high OM content, low pH, and consequently high weathering rates. A dramatic increase in spruce volume in the catchment of Lake Bolmen, illustrating a landscape wide shift from an agricultural to a forestry dominated land-use, was a strong predictor of long-term increases in Fe concentration in the lake. Moreover, increasing accumulation rates of Fe, Si and OM in more recent sediments of Lake Bolmen are in line with increased weathering and catchment loading in response to afforestation.

Increases in precipitation could promote catchment export through increased runoff and water saturation of soils that favor reductive dissolution and mobilization of Fe. Accordingly, catchment loading of Fe was positively correlated to flow to Lake Bolmen. However, variation in precipitation seemed to explain short-term variability in Fe concentrations and loading, rather than long-term trends.

Analyses of monitoring data further revealed a significant relationship between the increase in Fe concentrations and declining sulfate concentrations. However, when the role of S availability was investigated in the more mechanistic studies of this thesis, higher aqueous Fe concentrations were not found in response to lower S. In a microcosm experiment with soil slurries, Fe mobilization was in fact larger in treatments with high sulfate, probably due to increased acidity enhancing Fe solubility. Moreover, in sediment records of Lake Bolmen, Fe accumulation and the contribution of FeS were independent of elevated S accumulation during peak S deposition.

Collectively, the results of this thesis point to the importance of increased loading in response to afforestation and enhanced weathering, as a driver of increasing Fe concentrations. Increasing precipitation may further enhance Fe mobilization from coniferous forest soils.

Key words: Iron (Fe), freshwaters, browning, organic matter, biogeochemistry

Classification system and/or index terms (if any)

Supplementary bibliographical information		Language: English
ISSN and key title		ISBN 978-91-7895-336-3
Recipient's notes	Number of pages 148	Price
	Security classification	

Signature  Date 2019-10-24

Drivers of increasing iron concentrations in freshwaters

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LUND
UNIVERSITY

Coverdesign by Vidar Holje

Faculty of Science
Department of Biology

ISBN 978-91-7895-336-3 (print)
978-91-7895-337-0 (pdf)

Printed in Sweden by Media-Tryck, Lund University
Lund 2019

To my family

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List of Papers

In this thesis the papers are referred to by the following roman numerals:

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Author Contributions

I. CB, EK and GW developed the original idea and designed the study. CE, MG, H-PG, KK, IK, PK, HL, JL, NL, DM, PN, TN, FO, GR, JR, AR, JS, SS provided data for the study. CB performed the data treatment and analyses, except for the PLS analysis that was carried out by GW. CB wrote the manuscript with support from EK and GW. All authors provided comments on the manuscript drafts.

II. CB, MS and EK developed the original idea and designed the experiment. MS collected the soil, and MS and CB set up and ran the experiment and collected the data. DF performed the fungal identification. CB analyzed the data and wrote the manuscript with support from all authors.

III. CB and EK developed the idea and designed the study. CB carried out the field and lab work, as well as collected and analyzed the monitoring data. CB and PP collected the XAS data, PP performed the data treatment, and CB and PP analyzed the XAS data. CB wrote the manuscript with contributions from EK and GW. All authors commented on the manuscript drafts.

IV. CB and EK developed the original idea and designed the study. CB, EK and DH carried out the field work. CB performed the lab work and collected the monitoring data. CB, DH, and PP collected the XAS data, PP performed the data treatment, and CB and PP analyzed the XAS data. CB analyzed the monitoring data, except for the SLS that was performed by GW. CB wrote the manuscript with contributions from GW and EK. All authors provided comments on the manuscript drafts.

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Populärvetenskaplig sammanfattning

På senare år har flera studier visat på att järnhalten ökar i sjöar och vattendrag i norra Europa. Järn spelar en nyckelroll i akvatiska miljöer genom att påverka tillgängligheten av andra näringsämnen i vattnet så som kväve och fosfor, vilket kan reglera tillväxten av växtplankton. Dessutom färgar järn tillsammans med organiskt material vatten brunt. När vattnet blir brunare försämras ljusklimatet i sjön, vilket påverkar undervattensväxter och vattenlevande djur som är beroende av sin syn för att lokalisera byten. Vidare baseras dricksvattenproduktionen i Sverige i stor utsträckning på råvatten från sjöar. Att vattnet blir brunare kan få stora konsekvenser då vattenreningen blir mer komplicerad och kostsam. För att kunna säkra god vattenkvalitet är det därför viktigt att förstå varför järnhalterna ökar och dessa sötvatten blir brunare.

I denna avhandling undersökte jag om klimatförändringar mot ett varmare och våtare klimat, förändrad markanvändning med ökad andel barrskog, samt minskade mängder svavel i mark och vatten är möjliga orsaker bakom järnökningen. För att studera hur dessa komplexa processer påverkar järnets rörlighet i mark, vatten och sediment analyserade jag mönster i miljöövervakningsdata, utförde kontrollerade experiment, och använde sjösediment som arkiv över förändringar i miljö och vattenkemi över tid.

En ökad andel granskog i avrinningsområdet visade sig ha en hög förklaringsgrad när jag analyserade sambandet mellan järnkoncentrationer i vatten och granvolym. Under granskog bildas med tiden ett tjockt organiskt jordlager som försurar marken, vilket leder till vittring som frigör järn. Tillsammans med organiskt material kan järnet transporteras med markvatten till vattendrag och sjöar. Denna avhandling ger stöd för att en omfattande förändring i markanvändning, från ett mer öppet och jordbrukspåverkat landskap till ett mer tätbeskogat och barrdominerat, är en bidragande faktor bakom järnökningarna.

Jag fann också att järnhalter ökar i regioner där nederbörden ökat. En ökad nederbörd kan leda till en större transport av järn genom ökad ytavrinning från omgivande marker till rinnande vatten och sjöar. I linje med det fann jag att mer järn transporterades till en sjö under blöta år, och att mer järn frigörs när organiska och vattenmättade jordar är syrefria och reducerande. Trots detta förklarade variation i nederbörd bara korttidsvariationer i järnhalter och inte långsiktiga trender.

Slutligen fanns ett statistiskt samband mellan en ökning i järnhalt och en minskning i svavelhalt i de vatten jag undersökte. Eftersom svavel i reducerad form kan binda järn i mark och sediment skulle de ökade järnhalterna kunna vara ett resultat av en minskad bildning av järn-svavel-föreningar på grund av en minskad tillgång på svavel. När jag testade effekten av höga svavelkoncentrationer

på järnmobilisering från jord, fann jag emellertid inget stöd för en sådan mekanism.

Sammanfattningsvis fann jag att en utbredning av granskog är den troligaste orsaken bakom järnökningar i sötvatten, och att en ökande nederbörd kan bidra till att mer järn kan transporteras från skogsjordar. Med tanke på att en fortsatt ökning i järn och vattenfärg kan få allvarliga konsekvenser för ekosystemen och försämra vattenkvaliteten är det motiverat att vidare studera vad som driver denna förändring.

Brown water in a Swedish boral lake (Lake Strålsjön) (Photo: Caroline Björneråas).

Introduction

Iron (Fe) concentrations are increasing in freshwaters – i.e. lakes and running waters – in Sweden, as well as in other regions of the Northern Hemisphere. Together with increasing concentrations of dissolved organic matter (DOM), Fe is coloring the water and is thereby contributing to the ongoing browning of freshwaters, a phenomenon often referred to as 'brownification' (Fig. 1). The fact that freshwaters are becoming browner is of great concern. Long-term browning has serious ecological consequences (Solomon et al. 2015, Williamson et al. 2015, Creed et al. 2018), as well as implications for eco-system services (Kritzberg et al. 2019), including drinking water production that may become more complicated and costly (Matilainen et al. 2010). While the drivers behind increasing DOM concentrations in freshwaters have been extensively studied, little is known about what is causing Fe increases. The overall aim of this thesis is to understand what is driving the rising Fe concentrations in freshwaters.

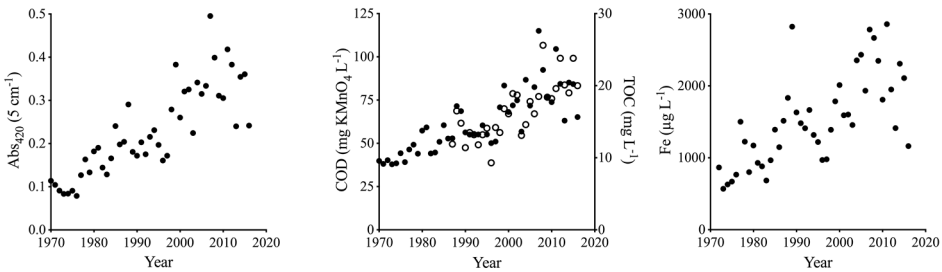

Figure 1. Example of freshwater that exhibit browning with increased water color (as absorbance at 420 nm), organic matter (COD and TOC concentration), and Fe concentration (River Helgeån, southern Sweden). The data is downloaded from the Swedish University of Agricultural Sciences (SLU) open database (SLU 2019).

The role of Fe in aquatic systems

One of the early reports of long-term trends was from the UK showing nearly a doubling in Fe concentrations in forest streams over 22 years of monitoring (Neal et al. 2008). The same magnitude of increase was found for Swedish rivers over a time period of nearly 40 years (Kritzberg and Ekstrom 2012). Increases have also been observed in Swedish lakes (Weyhenmeyer et al. 2014), where positive trends have been shown to be slightly more pronounced in the south than in the north of Sweden (Huser et al. 2011). Furthermore, increasing Fe concentrations have also been reported for Finnish streams (Sarkkola et al. 2013) and Northeastern Bavaria (Knorr 2013).

Increasing Fe concentrations have received attention mainly for its role in browning. Browning is often attributed to increasing concentrations of DOM absorbing short wavelength solar radiation in the visible range (Granéli 2012). However, Fe also contributes to color in freshwaters (Maloney et al. 2005, Kritzberg and Ekstrom 2012, Xiao et al. 2015), and the presence of Fe(III) is known to interfere with spectroscopic measurements (ultraviolet and visible light absorbance) of DOM concentration and composition (Doane and Horwath 2010, Poulin et al. 2014). Browning of freshwaters is thus also an effect of increasing Fe concentrations (Forsberg 1992, Kritzberg and Ekstrom 2012, Sarkkola et al. 2013, Weyhenmeyer et al. 2014).

Fe is important to aquatic systems in many other ways than by affecting color. Fe is in fact a key element in aquatic systems due to its high reactivity. It functions as a catalyst in fundamental biological processes such as respiration and photosynthesis (Wetzel 2001), and is an essential micronutrient to all organisms with very few exceptions (Beard et al. 1996). Fe has been identified as a limiting element to primary producers in marine waters (Martin and Fitzwater 1988, Boyd 2007, Kintisch 2007), as well as in freshwaters with low concentrations of bioavailable Fe (Twiss et al. 2000, Hyenstrand et al. 2001, Sterner et al. 2004, Vrede and Tranvik 2006). Moreover, the Fe cycle is tightly coupled to the biogeochemical cycling of other major elements (C, P, N, S), strongly affecting the fate of these elements in aquatic environments (Emerson et al. 2012).

The statement that ‘Fe is the most ironic of elements’ (Emerson et al. 2012) refers to the fact that despite being the fourth most abundant element in the Earth crust, low concentrations are usually found in natural waters. This is due to the low solubility of Fe(III) under oxic and circum-neutral pH conditions (Stumm and Morgan 1996). Fe(III) forms oxides and hydroxides (Fe-(oxy)hydroxides), such as ferrihydrite and more crystalline forms (e.g. goethite and hematite), that are prone to settle as particles. However, the complexation of predominately Fe(III) (Jansen et al. 2002) with DOM has been suggested to suppress the hydrolysis and precipitation of Fe(III) (Karlsson and Persson 2012), and hence to stabilize Fe in

freshwaters (Theis and Singer 1974, Perdue et al. 1976, Cameron and Liss 1984). In addition to these mononuclear Fe species in complex with organic matter (Fe-OM), Fe-(oxy)hydroxides associated with organic matter through surface interactions are abundant in natural waters (Andersson et al. 2006, Breitbarth et al. 2010, Raiswell and Canfield 2012, Sundman et al. 2014). Since both of these interactions with DOM increases Fe solubility, Fe and DOM concentrations usually co-varies in freshwaters (Kritzberg and Ekstrom 2012, Weyhenmeyer et al. 2014, Björnerås et al. 2017).

The tight coupling between Fe and C cycling in aquatic systems is also reflected in a strong control of Fe on OM bioavailability, mineralization, and subsequently CO_2 release to the atmosphere. Co-precipitation of Fe and DOM triggers sedimentation and removal of OM from the water column, where much of the mineralization occurs (von Wachenfeldt et al. 2008). In boreal lake water, Fe associated with DOM has been shown to inhibit bacterial growth by forming precipitates on bacterial surfaces and by limiting P bioavailability (Xiao et al. 2016). Moreover, association with Fe has been suggested to hinder microbial degradation of OM in marine and freshwater sediments, thus acting as a 'rusty sink' for storage of carbon (Lalonde et al. 2012).

The presence of Fe has also implications for cycling of nitrogen, phosphorus and sulfur (N, P and S). Fe is influencing N cycling by being as a co-factor in enzymes involved in nitrogen fixation, nitrification, as well as denitrification (Ferguson 1998). Since phosphate sorbs to the surfaces of Fe(III) phases, co-precipitation with Fe is a primary sink for P in waters (Slomp et al. 2013, Lenstra et al. 2018). Accordingly, Fe additions to increase P retention in lake sediments have been proposed as a measure to mitigate eutrophication (Smolders et al. 2006, Bakker et al. 2016). During reducing conditions, as in anoxic water and sediment layers, dissolved sulfate (SO_4^{2-}) is reduced to sulfide species (HS^-, H_2S) by bacteria (Berner 1984). These hydrogen sulfide may react with Fe(II) and form poorly soluble Fe sulfides (FeS – FeS_2) (Engstrom and Wright 1984).

While Fe is essential for ecosystem functioning, high Fe concentrations may have negative implications for aquatic systems. For instance, reduced light penetration as a consequence of browning may cause shifts in community composition (Weyhenmeyer et al. 2004, Grubisic et al. 2012, Ekvall et al. 2013), food-web structure (Wissel et al. 2003, Hansson et al. 2013) and impair primary production (Karlsson et al. 2009). Higher Fe concentrations may also promote cyanobacterial dominance and bloom formation, since cyanobacteria have higher Fe requirements than eukaryotic algae (Brand 1991, Molot et al. 2010). Furthermore, Fe could be harmful to organisms in high concentrations, e.g. to brown trout where gill damage and reduced oxygen uptake has been observed at exposure to high concentrations of Fe(II) and Fe(III) (Peuranen et al. 1994, Dalzell and Macfarlane 1999). Finally, reactive Fe-(oxy)hydroxides adsorb and co-precipitate toxic metals such as Cd and

Pb (Daviescolley et al. 1984), and may function as a vector that enhance the mobilization of heavy metals and organic compounds (Wallstedt et al. 2010).

From source to sink in the landscape

Understanding of why Fe concentrations are increasing in freshwaters requires knowledge of what controls Fe mobility in the landscape. Catchment soils are the main source of Fe in freshwaters, and ultimately weathering of minerals in the bedrock where Fe is abundant. However, as previously mentioned, the solubility of Fe in natural waters is generally poor and highly dependent on its speciation, with Fe(II) and organically complexed Fe being the more mobile Fe phases in natural waters. As Fe speciation is affected by pH, redox conditions and OM availability, these exert a major control on Fe mobility in the landscape (Fig. 2).

In boreal soils, the mobility of Fe in the upper organic layer is usually high due to a low pH and high availability of organic matter for complexation. In the process of podzolization, Fe is complexed by organic acids, transported downwards, and precipitated in the mineral soil layers where pH is higher (Lundstrom et al. 2000). As these pH and OM gradients contribute to a heterogeneity in Fe content, Fe concentrations in runoff are likely higher when soil layers enriched in Fe are being flushed. Furthermore, Fe solubility is enhanced in water-logged soils, such as peatlands, where decomposition of OM depletes oxygen and promotes reduction to Fe(II).

The interface between the terrestrial landscape and streams is referred to as the riparian zone in boreal landscapes, which is ultimately a zone rich in organic matter, and Fe, where groundwater passes through before discharging into the stream (Lidman et al. 2017). Elevated Fe concentrations in this zone could be explained by a low pH, high water saturation, and high availability of DOM for complexation (Lidman et al. 2017). Although Fe precipitation is expected to occur in the transition from anoxic groundwater to oxic stream water (Duckworth et al. 2009), complexation with OM may facilitate the passage of Fe through this redox barrier into freshwater systems. Accordingly, organically complexed Fe has been shown to be the dominant phase in boreal headwater streams (Sundman et al. 2014, Herzog et al. Discussion paper for Biogeosciences).

Variability in pH, redox, and OM availability has furthermore an impact on the distribution of Fe within freshwaters, e.g. in oxic-anoxic interphases in the water column and sediments (Davison 1993). The main pathways for Fe losses in lakes are via sedimentation and discharge out of the lake (Maranger et al. 2006), the former induced by hydrolysis and aggregation of Fe-(oxy)hydroxide particles, which is enhanced at higher pH (Neubauer et al. 2013), and flocculation together with DOM (von Wachenfeldt et al. 2008). However, although Fe may settle together with OM in lakes, the association with organic matter is a prerequisite for Fe to remain in solution in oxic circum-neutral waters. For example, surface interactions with OM give inorganic Fe colloids a negative charge, which will slow down aggregation and subsequent sedimentation (Wetzel 2001). Moreover,

organically complexed Fe has been shown to be more stable against pH and salinity induced aggregation than Fe-(oxy)hydroxides in estuarine salinity gradients (Herzog et al. 2017).

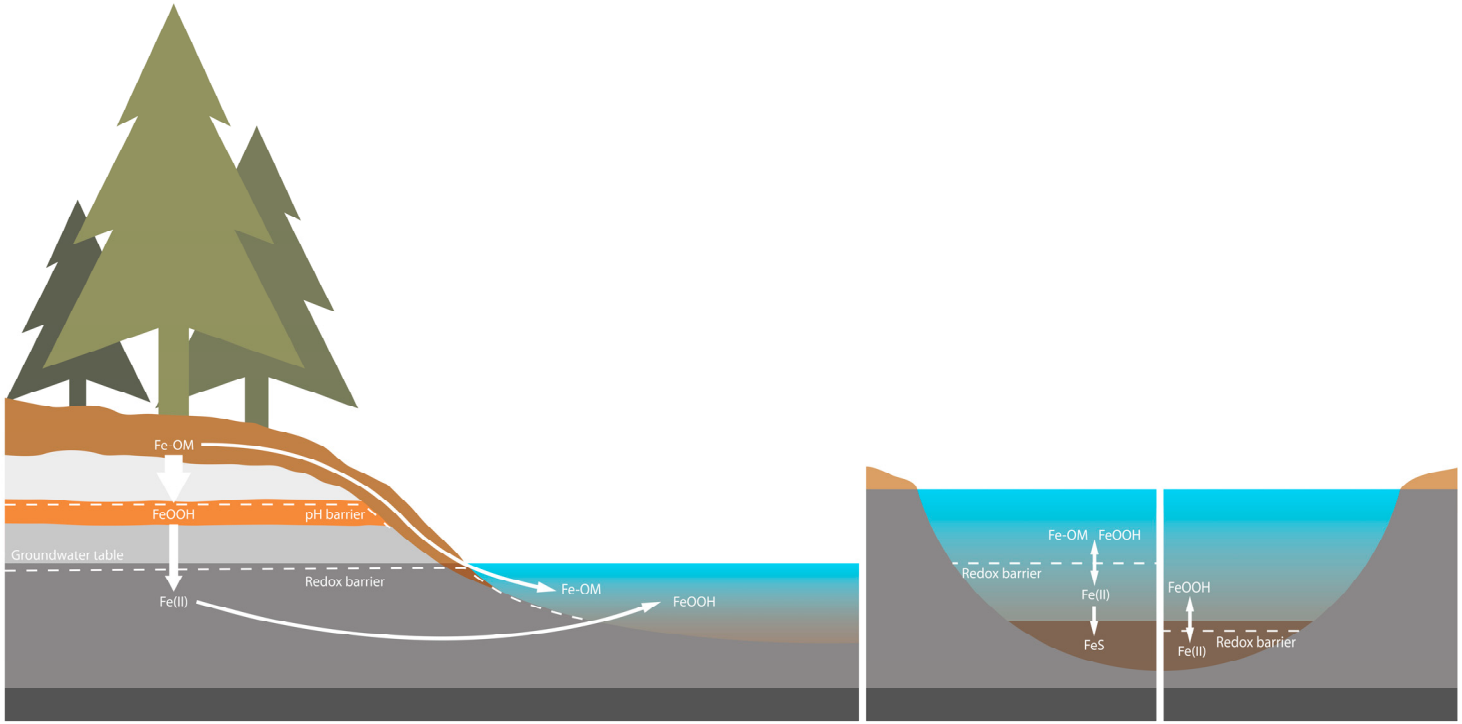

Figure 2. Mobilization barriers (pH, redox, DOM) controlling Fe mobility a boreal soil and riparian zone (left), as well as in a lake during stratified and mixed conditions (right).

Potential drivers behind increasing Fe concentrations

The observed Fe trends in freshwaters can be the result of two principally different processes; increasing Fe export from the terrestrial catchment and/or changes in biogeochemical cycling of Fe within the aquatic continuum. Both of these processes are potentially affected by changes in climate, atmospheric S deposition, and land-use (Fig. 3).

Precipitation increases following climate change

Climate change, expressed as altered precipitation patterns and higher temperatures, affects the hydrology and redox conditions in catchment soils. Increased precipitation, which is both recorded and further predicted for many northern regions (Nikulin et al. 2011), can affect Fe export from the catchment by sheer increase of the runoff, i.e. larger influxes. Since increased precipitation may enhance weathering of catchment soils containing Fe (White and Blum 1995), there is a potential for larger Fe loads from the catchment to aquatic systems during high flow. Furthermore, higher precipitation may result in raised groundwater tables and flow through more superficial and organic rich soil layers (Hongve et al. 2004, Haaland et al. 2010), and give increased transport of high molecular weight DOM fractions with a high affinity for Fe (Forsberg 1992, Riise 1999).

A wetter and warmer climate may also promote reducing conditions in soils and reductive dissolution of Fe(III). Reductive dissolution of Fe-(oxy)hydroxides (together with DOM release) has been observed in wetland soil incubations (Grybos et al. 2007), and has been suggested to control Fe mobilization in wetlands in field studies (Knorr et al. 2009). Accordingly, an observed drop in Fe concentrations in streams and catchment fluxes of Fe during dry periods have been attributed to Fe oxidation and immobilization when the water table is lowered in boreal catchments (Dillon and Molot 2005, Landre et al. 2009).

Fe concentrations in freshwaters are further controlled by in-lake processes, such as aggregation and sedimentation. Higher precipitation leads to faster flushing rates through lakes, and hence shorter water residence times (WRT). This gives Fe colloids less time to aggregate and sediment (Weyhenmeyer et al. 2014), and results in that more Fe may remain in the water column. Fe sedimentation has been shown to be positively related to water residence time in Swedish lakes (Borg et al. 1989, Kohler et al. 2013).

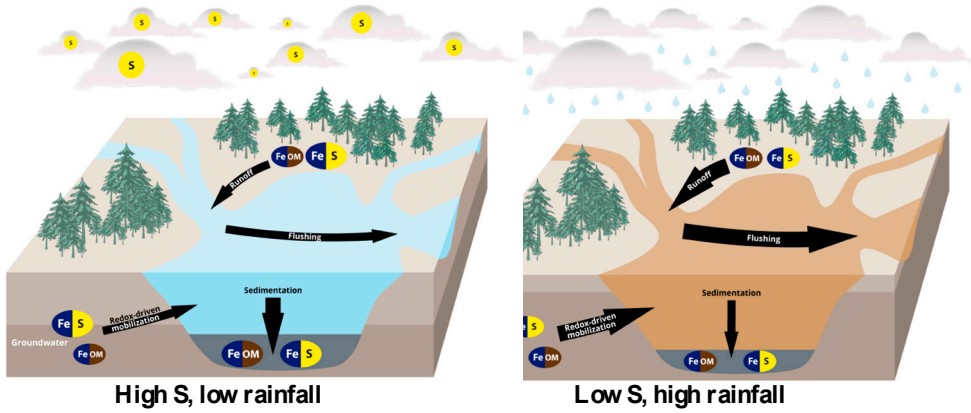

Figure 3. Under a high S deposition scenario, Fe binding to sulfides could reduce Fe export from catchment soils to surface waters, and result in more Fe sulfide accumulation in sediments (left). In a wet-climate scenario with less reactive S, more intense precipitation increases runoff from the catchment, flushing rates through lakes, and redox-driven mobilization of Fe in the soils as a result of a raised groundwater table (right).

Declining atmospheric S deposition

The long-term reduction in sulfate deposition (mainly in anthropogenic S emissions) since the 1980s (Schopp et al. 2003), followed by a recovery from acidification in forest soils (Akselsson et al. 2013), and a decrease in sulfate concentration in freshwaters (Garmo et al. 2014), may be another factor driving the increasing Fe concentrations in freshwaters. The fact that sulfate deposition has declined during the past decades may have enhanced Fe mobilization due to less Fe sulfide formation, increased Fe reduction, and increased DOM availability.

As described previously, formation of stable Fe sulfides can potentially immobilize Fe in reducing soils (Bottrell et al. 2007), as well as in the sediments of lakes (Engstrom and Wright 1984, Nurnberg and Dillon 1993). Reduced inputs of S has also been suggested to increase Fe reduction by shifting anaerobic respiration towards Fe reduction (Knorr 2013), since Fe and sulfur reducing bacteria have been shown to co-exist and to compete for organic substrates (Chapelle and Lovley 1992). Hence, it is possible that lower sulfate concentrations, and subsequently lower sulfate reduction rates, may have contributed to reduction of Fe(III) to the more mobile Fe(II). Furthermore, an increase in soil pH following a decrease in atmospheric S deposition may have influence Fe mobility in catchment soils. On one hand, lower pH – as during peak S deposition – enhances Fe solubility and weathering rates (Sulzberger et al. 1990). On the other hand, low pH reduces OM solubility (Ekstrom et al. 2011), and subsequently the mobility of Fe-OM complexes (Neal et al. 2008, Fang et al. 2015).

Land-use changes in the catchment

Recent vegetation expansion and land-use changes, including a transition from a more open landscape heavily influenced by agriculture to a dominance of coniferous forest, has been put forward as an important driver behind the browning of freshwaters in Fennoscandia (Finstad et al. 2016, Kritzberg 2017). This rapid and drastic shift in vegetation from mixed or broadleaf species to conifers is caused by a reduction in grazing by domestic animals and forest plantation, and has happened during the last century in southern Sweden (Fredh et al. 2012, Lindbladh et al. 2014), as well as in North America (Houghton et al. 1999).

Water color in freshwaters is known to be strongly dependent on land cover, and the proportion of coniferous forest and wetland in the catchment are good predictors of Fe and DOM concentrations (Dillon and Molot 1997, Kortelainen et al. 2006, Mattsson et al. 2009). Increasing Fe and DOM concentrations in soil solutions in response to coniferous afforestation has been observed (Hughes et al. 1990), due to the slow build-up of organic carbon pools that can leach organic matter to connected streams (Kritzberg 2017). The organic acids produced are furthermore likely to enhance soil weathering and the complexation of Fe. Increasing weathering rates have been shown to follow increases in vegetation cover, and the proportion of forest and wetland areas (Humborg et al. 2004). Although land-use change, and in particular afforestation, has great potential to alter weathering rates and mineral export, this has received little attention as a potential driver of increasing Fe concentrations in freshwaters.

Aims and objectives of the thesis

The main aim of this thesis was to further our understanding of what is causing Fe concentrations to increase in freshwaters of the Northern Hemisphere. The increase in Fe concentrations could be the result of influx from surrounding soils and/or the result of changes in the biogeochemical cycling of Fe within the aquatic continuum. I have looked into how both of these processes are linked to changes in climate, atmospheric sulfate deposition, and land-use changes. Since Fe concentrations in freshwaters are controlled by mobilization and immobilization processes – both on land and in the water – this thesis includes studies of processes in soil, water and sediments. Moreover, the thesis is based on a wide range of scientific approaches, including controlled mechanistic experiments in microcosms, an Fe mass balance of a lake, analysis of Fe speciation in different compartments (inflowing and outflowing water and sediments), interpretation of sediment records in light of variation in water chemistry and environmental variables, and analysis of temporal and spatial patterns in Fe concentrations from monitoring data of wide geographic distribution.

Hypotheses

I. Fe concentrations are increasing in freshwaters due to a reduction in atmospheric sulfate deposition resulting in;

   A. Increased catchment Fe export due to a reduction in FeS formation in soils, and a higher availability of DOM for complexation (Paper I, Paper II).

   B. Lakes being less efficient Fe sinks due to a reduction in FeS formation in sediments (Paper I, IV).

II. Fe concentrations are increasing in freshwaters due to increased precipitation resulting in;

   A. Increased catchment Fe export due to wetter and more reducing conditions in the catchment soils, which favor Fe reduction and mobility (Paper I, II).

   B. Lakes being less efficient Fe sinks due to faster flushing rates, which diminish Fe loss to sediments (Paper I, Paper III, Paper IV).

III. Fe concentrations are increasing in freshwaters due to afforestation resulting in increased Fe export from boreal soils (Paper I, Paper IV).

Methodology

The scientific approaches and methods applied to test the above hypothesis in the four papers of this thesis are described briefly in the following sections.

Paper I

Temporal trends of Fe concentrations across 340 water bodies distributed over 10 countries in northern Europe and North America were examined in order to gain a clearer understanding of where, to what extent and why Fe concentrations are on the rise. Trends were assessed using the Mann-Kendall trend test on monitoring data. Spatial and temporal patterns in Fe concentrations, sulfate concentrations, precipitation and boreal forest cover in the catchment were explored to identify potential drivers behind Fe trends, and if there were geographical differences in trend drivers. Partial least squares (PLS) regression was used to predict variance in relative changes in Fe concentration with water chemistry, climate and catchment variables as explanatory variables.

The non-parametric *Mann-Kendall trend test* is used to assess if a variable (Y) tend to increase or decrease (monotonic change) over time (X) (Helsel and Hirsch 2002), and is commonly applied to environmental data since it is robust and can cope with missing values, as well as values below a detection limit. The Mann-Kendall test has been used previously to detect trends in monitored freshwater Fe concentrations over time (Neal et al. 2008, Kritzberg and Ekstrom 2012, Sarkkola et al. 2013, Weyhenmeyer et al. 2014), and is often combined with the Theil-Sen estimator which derives the slope, i.e. the rate of change, of the trend (Theil 1950, Dery et al. 2009, Stahl et al. 2010).

PLS ranks explanatory variables according to their relevance in explaining variation in the response variable, and it can analyze data with multiple, as well as correlated, explanatory variables (Wold et al. 2001).

Paper II

How Fe mobilization in water-saturated soils is regulated by redox conditions (anoxic vs oxic conditions), and the availability of sulfur, was studied in this mechanistic soil incubation study. The effect of these mobilization barriers was

assessed by applying high (peak S deposition) and low (present day) sulfate treatments and oxic versus anoxic conditions to microcosms. Incubations lasted for 134 days and the Fe mobilized from soil into the aqueous phase was monitored.

Although soil microcosm incubations do not entirely encompass the complexity of natural soil systems, this approach is efficient to study biogeochemical processes in a simplified and controlled setting. Soil incubations have been shown to be useful for studying Fe fluxes during shifting redox conditions (Schuth et al. 2015), and to explore the interaction between Fe and S in soils (Yu et al. 2007, Vink et al. 2010).

Paper III

The function of the lake as a sink for Fe, and how that may be connected to Fe speciation and short-term variations in precipitation and water residence time was assessed in Lake Bolmen, southern Sweden (Fig. 4). Mass-balance analyses (lake influxes – outfluxes), to evaluate the loss of Fe within the lake, were performed based on monitoring data of Fe concentrations and water flow in inflowing and outflowing water for the period 2010-2018. Furthermore, the loss of Fe to the sediments was estimated from Fe accumulation rates in the lake sediments. Fe accumulation rates were based on Fe concentrations (ICP-OES on digested samples) in ^{210}Pb dated sediments. The radionucleotide ^{210}Pb has a known decay rate (half-life of 22.3 years) in the environment, and is therefore useful in dating of recent sediments (Appleby 2008). How aqueous Fe concentrations, and the loss of Fe to sediments, are related to precipitation patterns, and consequently to variation in water residence time of the lake, was evaluated from long-term monitoring data of Fe concentrations in combination with climate data.

Figure 4. Satellite image of Lake Bolmen in southern Sweden (left; Copernicus Sentinel data, 2019, by Brockmann Geomatics), and a photo of one of the main lake tributaries (right; the outlet of Lake Unnen, photo: Caroline Björneås). The lake is a source of drinking water supplying more than 500 000 citizens with drinking water. The water color has increased strongly in the lake since the 1970's (Kritzberg 2017).

Analyses of Fe speciation by *X-ray absorption spectroscopy (XAS)* in inflowing and outflowing water, and in surface sediments was used to explore how Fe speciation affects the fate of Fe within Lake Bolmen. We used the technique to distinguish between Fe-(oxy)hydroxides and organically complexed Fe as the latter Fe phase is known to have a higher stability in oxic circum-neutral waters, whereas Fe-(oxy)hydroxides are expected to be more prone to sediment. XAS is a useful tool for characterizing bonding environments of metals in complex natural environments, and the technique has previously been used to study Fe speciation and the interaction with OM (Karlsson and Persson 2010, Karlsson and Persson 2012, Sundman et al. 2014, Herzog et al. 2017).

Linear combination fitting (LCF) analyses were used to determine the relative proportion of Fe-(oxy)hydroxides and organically complexed Fe, as well as to identify other potential Fe phases in the lake water and sediment samples. LCF analyses were performed by fitting sample spectra from the extended X-ray absorption fine structure (EXAFS) region with reference spectra of Fe-(oxy)hydroxides, organically complexed Fe, Fe clay minerals, as well as Fe sulfides. Differences in Fe-(oxy)hydroxides and organically complexed contributions between samples were further confirmed using the wavelet transformation (WT) method, which is a qualitative interpretation of the EXAFS data providing information on the nature of backscattering of atoms in higher coordination shells (Fig. 5).

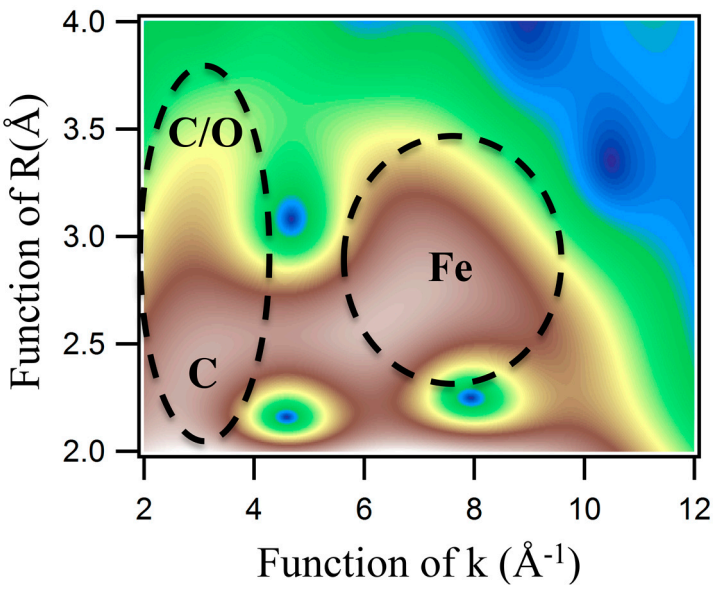

Figure 5. High resolution wavelet transformation (WT) plot (η=4 and σ=2) obtained from EXAFS spectra of a sample from the main inlet to Lake Bolmen. The area representing Fe paths indicative of organically complexed Fe (C and C/O) and Fe-(oxy)hydroxides (Fe) are highlighted.

Paper IV

The focus of this study was the role of the declining S deposition on sediment binding of Fe (through FeS formation) in Lake Bolmen. A paleolimnological approach was applied to study the impact of changes in sulfate deposition on Fe accumulation rates and Fe speciation in ^{210}Pb dated sediment cores. Fe speciation was determined with XAS applying LCF analyses on EXAFS data, as described for Paper III, to identify FeS phases. The elemental composition of the Lake Bolmen sediments was further analyzed with X-ray Fluorescence Spectroscopy (XRF) to assess changes in catchment derived elements such as Si and K, as well as Fe, as indicators of erosion and catchment weathering. The paleolimnological record was complemented with long-term data records of water chemistry, sulfate deposition and other potentially relevant environmental drivers of increasing Fe concentrations (temperature, precipitation, coniferous afforestation).

XRF is a rapid, non-destructive technique based on the detection of element-specific fluorescence (secondary X-rays) emitted from atoms excited by incident X-rays (Boyle 2000). Hence, since the secondary X-rays generated during XRF scanning will be characteristic of the elements present, as well as their abundances, the method provides information about the chemical composition the sample.

Lake sediments have frequently been used to reconstruct past environmental conditions (Engstrom and Wright 1984), to study the impact of climate change (Catalan et al. 2013), as well as to provide reliable records of atmospheric pollutants (Boyle et al. 2004, Bindler et al. 2008) and metal accumulation (Couillard et al. 2004, Backstrom et al. 2006, Grahn et al. 2006). Thus, sediment dating along with analyses of Fe concentration and speciation in sediments may provide useful information of past accumulation rates of Fe, and therefore reveal how the role of lakes as Fe sinks have changed. Although post-burial redox mobilization and upward diffusion of reduced Fe may complicate the interpretation of past changes in the lake (Boyle 2001), a high sedimentation rate reduces the risk of significant remobilization (Boyle et al. 2004). Furthermore, the presence of sulfides may as previously mentioned play a role in immobilizing Fe in the sediments as FeS (Huerta-Diaz et al. 1998, Nordmyr et al. 2008).

Main results

Temporal and spatial trends in Fe concentration (Paper I)

This study was the first to demonstrate that strong increases in Fe concentrations is a widely distributed phenomenon. Fe was increasing in 28 % of the studied water bodies with a median increase of 61 % between 1990 and 2013, while a significant decrease was observed in 4 % of the study systems (Fig. 6). Positive trends were more frequent in the European (39 %) than in the included North American systems (9 %). The relative rate of increase in Fe concentration was significantly higher in headwaters than in higher-order streams and river mouths, as well as in lakes compared to streams. This may indicate that increased catchment export along with a declining efficiency of lakes as Fe sinks are contributing to the observed positive Fe trends.

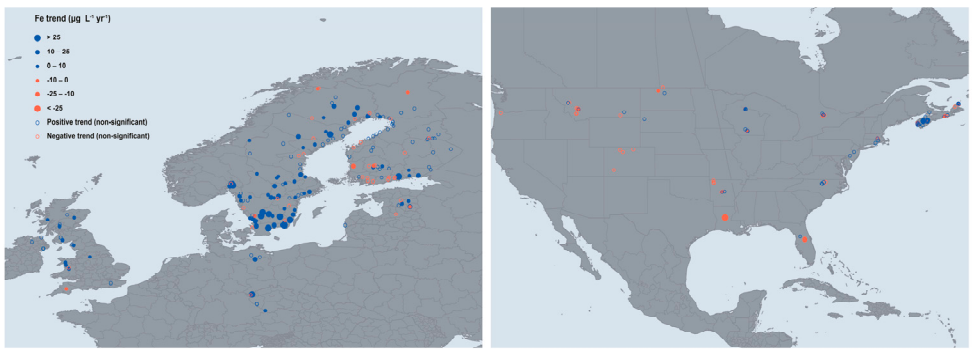

Figure 6. Changes in Fe concentration in (left) European and (right) North American freshwaters between 1990 and 2013. Blue circles represent positive and red circles represent negative trends in Fe concentrations. The size of the circles reflects the magnitude of the changes. Filled circles denote significant trends, and open circles denote nonsignificant changes.

The large regional differences, with most of the positive trend sites located in boreal areas in Fennoscandia, could partly be explained by differences in precipitation changes over time. Regions with frequent positive Fe trends, were regions where precipitation had increased. Furthermore, positive trends were more frequent and occurring at a higher rate in catchments with a large cover of conifers. Although positive changes in Fe concentration were found to be correlated with a decline in sulfate, sulfate concentrations had decreased in most

systems, also in those water bodies with negative Fe trends (Fig. 7). Hence, the declined atmospheric S deposition may have contributed to increasing Fe concentrations, but is unlikely the sole explanation behind the trends.

Since DOC concentrations increased in most – but not all – water bodies with long-term increases in Fe concentration, an increases availability of DOC for complexation may have contributed to the observed Fe trends but could not have been the only driver. More likely, similar drivers had governed mobilization of both Fe and DOC, but increases in DOC *per se* were not driving Fe trends.

Controls on Fe mobility in a boreal soil slurry (Paper II)

I hypothesized that anoxic conditions would favor Fe release from soil to the aqueous phase in the microcosms, while sulfate concentrations were expected to suppress Fe mobility through FeS formation and/or by lowering pH and thereby DOC concentrations. In line with these expectations, I found that anoxia had a positive effect on Fe concentrations in solution, and high concentrations of Fe(II) suggested that reductive dissolution was the mechanism behind Fe mobilization (Fig. 8). In contrast to the hypothesis, Fe concentrations in solution were enhanced in treatments with high sulfate concentrations, although DOC concentrations were suppressed (Fig. 8). It was probably the high acidity in the high sulfate treatment that promoted the release of Fe. Fe mobilization was not limited by DOC availability in our systems where DOC was present in great excess compared to Fe at all times.

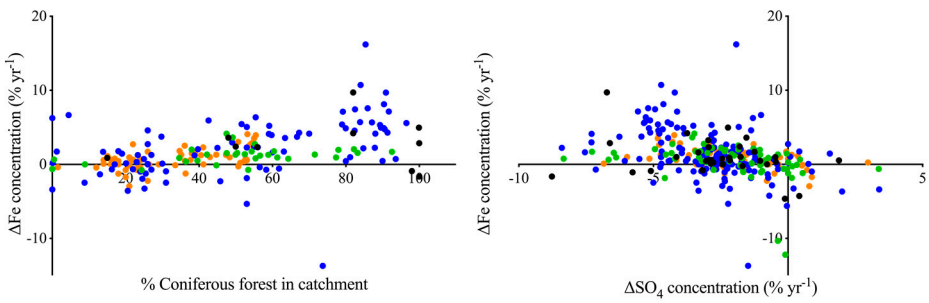

Figure 7. Relationships of relative change in Fe with percentage of coniferous forest in catchment and sulfate concentration. Symbols represent data for headwater streams (black), higher-order streams (green), lakes (blue), and river mouths (orange).

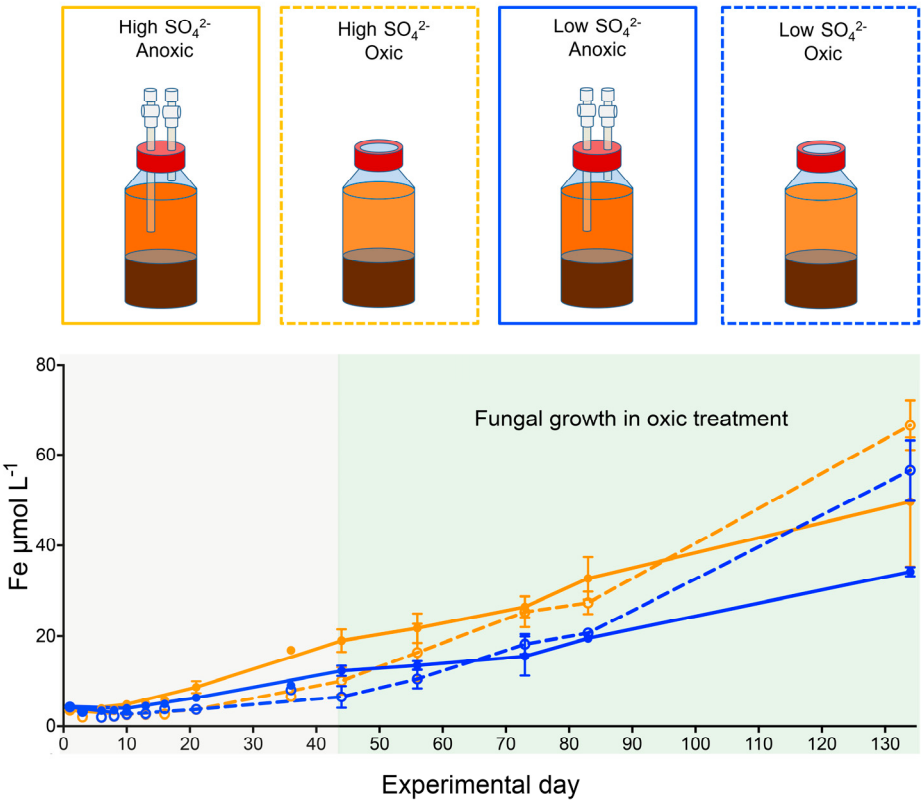

Figure 8. Overview of the four microcosm treatments in the upper panel (Design: Martin Škerlep). The lower graph shows mean Fe concentration in the four treatments over time. Results for high sulfuric acid treatments are shown as orange lines, low sulfuric acid treatments as blue lines, while oxic treatments and anoxic treatments are denoted by dashed and solid lines respectively. Error bars ± 1 SD. The green background highlights the period with the fungus *Jaapia ochroleuca* growing in the O treatments.

Unexpectedly, growth of the wood decaying basidiomycete fungus *Jaapia ochroleuca* was found in the oxic treatments 7 weeks into the experiment. The establishment of the fungus had a major impact on Fe mobilization, i.e. Fe concentrations in the oxic treatments exceeded those in the anoxic ones at the end of the experiment (Fig. 8). Hence, pH along with fungus-induced mobilization were the main factors controlling Fe concentrations in solution, confirming the importance of reducing conditions in soils, but offering little support to declining atmospheric S deposition as an important driver for increasing Fe mobilization.

Finally, while Fe is often presumed to precipitate in the barrier between anoxic soil water to oxic surface waters, Fe remained in suspension after introduction of oxygen, probably due to complexation by organic matter.

The importance of the lake as a sink for Fe (Paper III)

Fe concentrations and fluxes in to the lake exceeded by far Fe concentrations and fluxes out from the lake, supporting that Lake Bolmen is a major sink for Fe. On average, the Fe concentration in outflowing water was 77 % lower than that of outflowing water. A high accumulation rate of Fe in dated lake sediments corresponded well with estimated Fe losses from mass balance calculations (inflow flux – outflow flux) and confirmed the importance of the lake as a sink for Fe (Fig. 9).

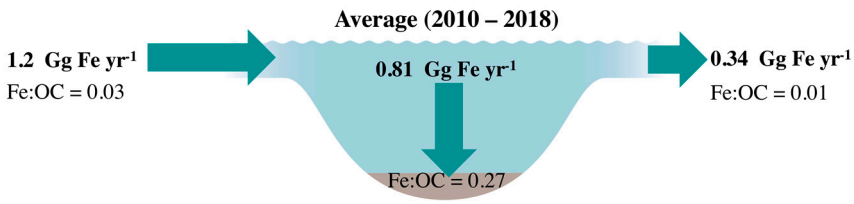

Figure 9. Mass balance model of Fe showing inflow fluxes, outflow fluxes and estimated loss to sediments (average for 2010 – 2018), as well as the molar Fe:OC ratios in inflowing water, outflowing water, and surface sediments deposited between 2010 and 2015.

Both water flowing in and out of the lake contained both organically complexed Fe (Fe-OM), Fe-(oxy)hydroxides (FeOOH) and Fe clays, but Fe-OM was not contributing significantly to Fe in the sediments (Fig. 10). The absence of Fe-OM in the sediments, indicated that the lake is mainly a sink for FeOOH and Fe clays (Fig. 10). A higher contribution of Fe-OM in inflowing than in outflowing water, indicate a transformation of Fe-OM to FeOOH within the lake. Most probably this transformation was promoted by increasing pH and photoreduction, and subsequent hydrolysis of Fe in the water column of the lake. However, it was interesting that the outflowing Fe was strongly dominated by FeOOH, which must have properties that keep it stable in the water column despite the long residence time of the lake (~1.6 years).

In theory, the lake may be less efficient as an Fe sink during periods of high precipitation and shorter residence time, which could constrain loss processes leading to sedimentation and result in higher water Fe concentrations. There was large within- and between-year variations in precipitation, Fe concentrations and fluxes. However, rather than smaller Fe losses, larger within-lake losses in Fe occurred wet years. This was probably because the main effect of high precipitation was a higher loading of Fe from the catchment. Thus, although the lake was found to be a major Fe sink, variation in precipitation and flow may influence Fe concentration in the water column more by affecting loading than losses to the sediments.

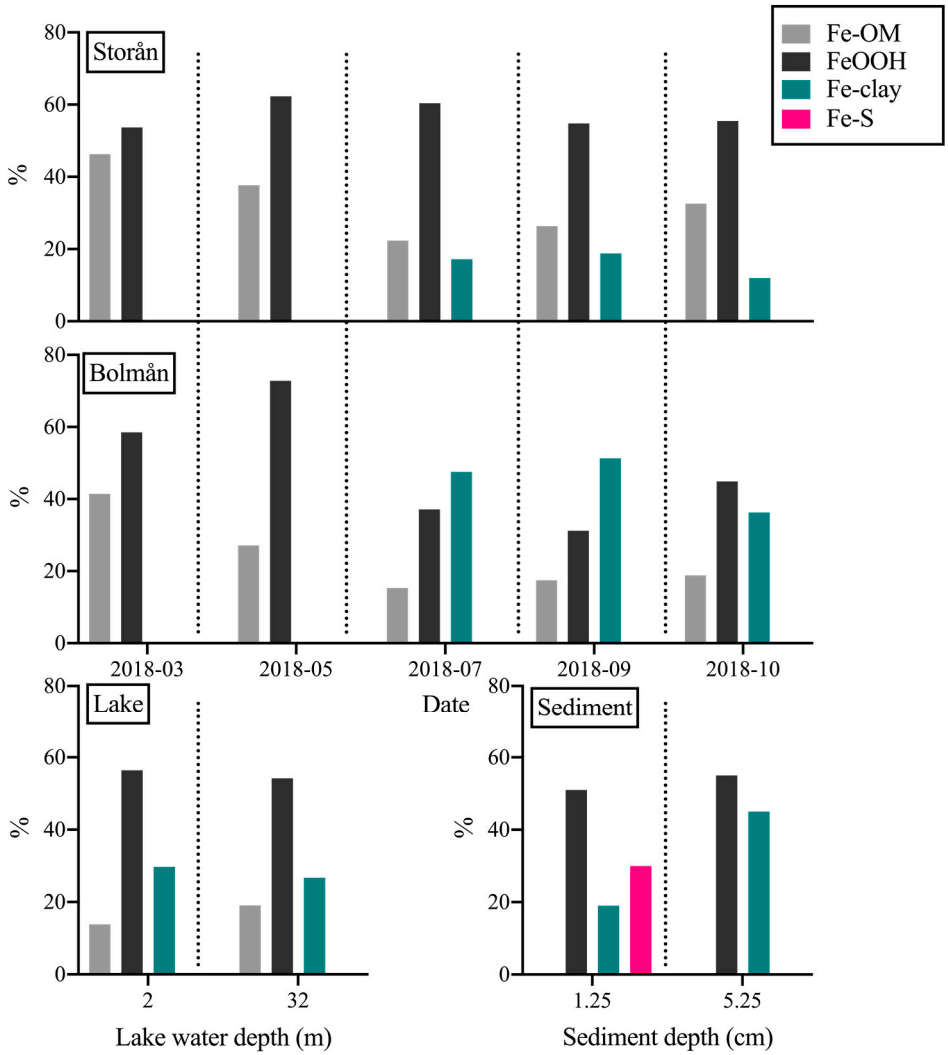

Figure 10. Fe speciation determined by XAS and linear combination fitting (LCF) with model compounds. Samples were collected in the main inlet Storån and in the outflow Bolmån during five sampling occasions from March 2018 to October 2018, in the lake water at two depths (October), and in two surface sediment samples deposited between 2010 and 2015. Organically complexed Fe (Fe-OM), Fe-(oxy)hydroxides (FeOOH), Fe clay and silicate minerals (Fe-clay), and Fe sulfides (Fe-S) were used as reference compounds and their relative contribution to the LCF models are presented (as %).

The role of atmospheric S deposition and FeS formation on aqueous Fe concentrations (Paper IV)

Long-term monitoring revealed that Fe concentrations, as well as water color, increased strongly in Lake Bolmen between 1966 and 2018 (by 98 % in the outlet) (Fig. 11). S deposition was a strong predictor of Fe concentrations in the outlet, at least during the period of declining deposition. Spruce volume in the catchment was also a significant predictor of long-term changes in Fe concentrations, while precipitation could explain short-term variations in Fe concentrations but not the long-term trend.

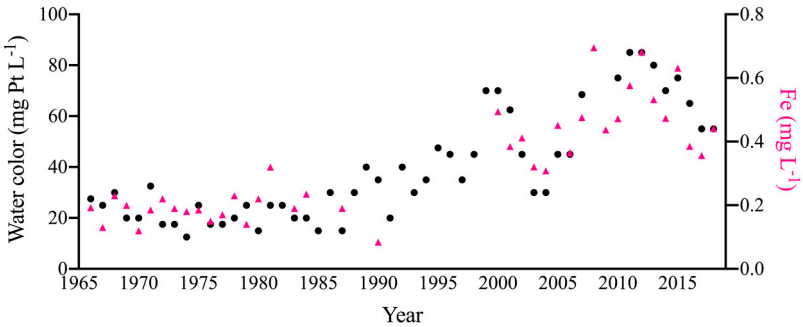

Figure 11. Increases in yearly median Fe concentration (pink triangles) and water color (black dots) at the outlet of Lake Bolmen between 1966 and 2018.

The sediment record showed elevated accumulation of S in sediments deposited during peak atmospheric S deposition, and the EXAFS analyses revealed a significant contribution of FeS in the sediments (Fig. 12). However, Fe accumulation rates in the sediments were independent on S accumulation and Fe speciation was dominated by Fe-(oxy)hydroxides together with Fe clay fractions at all studied sediment depths (Fig. 12). Hence, the sediment analyses give no support to the hypothesis that increases in Fe concentrations in the lake is due to less FeS binding in the sediments today compared to peak S deposition. Moreover, the accumulation rate of Fe in the sediments increased rather than decreased, suggesting that increasing Fe loading is more important to increasing Fe concentrations in the water, than a change in the relative distribution of Fe between the water column and sediments.

Spruce volume increased dramatically in the catchment, and the acidic organic soils that develop in coniferous forest may have higher weathering rates of Fe minerals. Also, the growing organic carbon stocks in response to forest growth may also be a significant source of organic matter for Fe complexation. The parallel increases in the accumulation rate of Fe, Si, Al and C in the sediments are in line with afforestation as an important driver of increasing Fe loading and aqueous concentrations due to enhanced weathering.

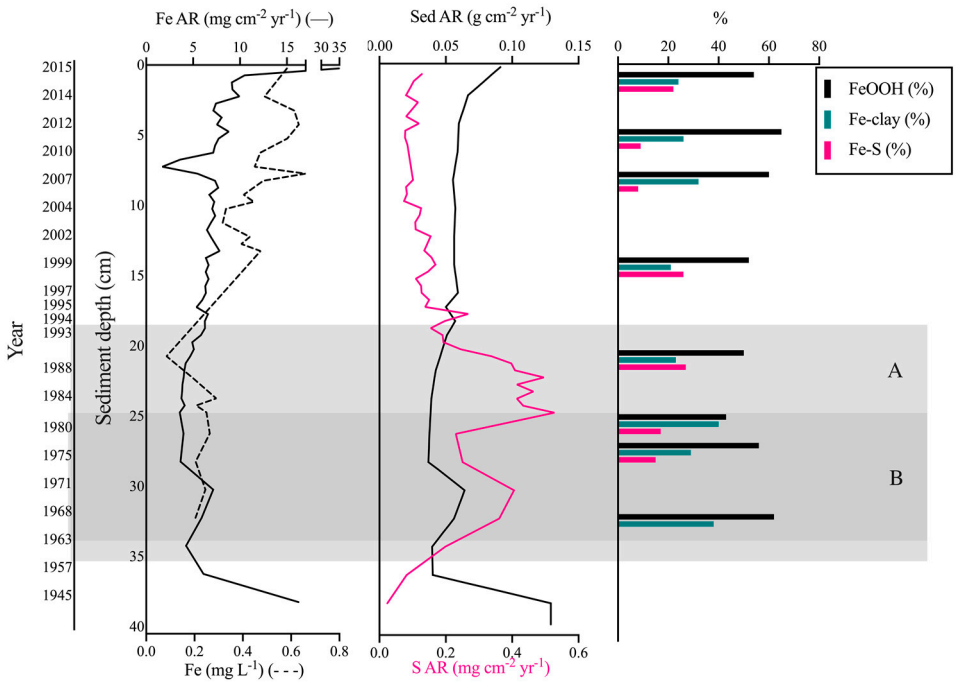

Figure 12. Dry weight sediment accumulation rates (Sed AR), and accumulation rates of Fe and S in the Lake Bolmen sediment profile dating back to 1943. The first graph also shows yearly mean Fe concentrations in water samples collected at the lake outlet between 1966 and 2015. Fe speciation based on EXAFS linear combination fitting (LCF) results for eight sediment samples are shown in the right panel. Organically complexed Fe (Fe-OM), Fe-(oxy)hydroxides (FeOOH), Fe clay and silicate minerals (Fe-clay), and Fe sulfides (FeS) were used as reference compounds and their relative contribution to the LCF models are presented (as %). The period with elevated S accumulation rates (A) and the period with a peak in SAR and Si accumulation (B) are highlighted in grey.

Conclusions and outlook

While there have been previous reports of increasing Fe concentrations in freshwaters (Neal et al. 2008, Kritzberg and Ekstrom 2012, Knorr 2013, Sarkkola et al. 2013, Weyhenmeyer et al. 2014), these have been spatially and oftentimes temporally restricted. Paper I was the first to establish that Fe concentrations are increasing on a wide geographical scale.

Analysis of monitoring data further revealed a significant relationship between the increase in Fe concentrations and declining sulfate concentrations (Paper I and IV). The decline in atmospheric S deposition and subsequent recovery from acidification has been proposed to be a main driver of increasing freshwater concentrations of DOM (Evans et al. 2006, De Wit et al. 2007, Monteith et al. 2007) and therefore to indirectly promote higher Fe concentrations (Neal et al. 2008). However, the fact that sulfate concentrations have decreased in the vast majority of systems included in this thesis, also in water bodies with negative Fe trends (Paper I), indicates that decreasing sulfate is not a sole driver of increasing Fe concentrations in freshwaters.

Furthermore, the studies targeting the mechanistic link between Fe and S failed to provide support for this hypothesis. In the microcosm experiment, rather than suppressing Fe mobilization, high sulfate concentrations had a positive effect on Fe mobilization, probably due to increased acidity enhancing Fe solubility (Paper II). Moreover, Fe accumulation – as well as Fe accumulated as Fe sulfides – was not elevated in the sediments of Lake Bolmen in response to higher S accumulation during peak S deposition (Paper IV). Hence, although FeS formation has the potential to immobilize Fe in reducing soils and sediments (Bottrell et al. 2007), this thesis offers little support to the hypothesis that rising Fe concentrations in freshwaters are due to less FeS binding in soils and sediments today compared to when S deposition was higher. It is possible that this process is relevant in other soil systems, e.g. in intact soil profiles possessing a higher complexity than soil slurries, or in lakes with different conditions. Future studies should distinguish between different source areas, e.g. wetlands and mineral soils, which may differ with regards to controls on Fe mobilization. Furthermore, future work could better address the indirect effect of declining S deposition on Fe concentrations by affecting pH and OM solubility.

The large regional differences in Fe trend patterns may be linked to differences in precipitation changes, since Fe trends were more frequent in regions where precipitation had increased (Paper I). Moreover, higher rates of increase in lakes than in running waters are indicative of the importance of in-lake processes for Fe losses. Faster flushing rates through lakes, driven by increasing precipitation, has been suggested to restrain Fe sedimentation and thereby result in higher Fe concentrations in the water column (Weyhenmeyer et al. 2014). The importance of lakes as Fe sinks was supported by high Fe accumulation rates in the sediments of Lake Bolmen, and by mass balance calculations illustrating that Fe fluxes in to the lake by far exceeded fluxes out of the lake (Paper III). However, while lakes were hypothesized to be less efficient as Fe sinks during higher precipitation, within-lake losses of Fe were larger during wet years in Lake Bolmen. Moreover, higher precipitation in the Lake Bolmen catchment resulted in higher catchment loads of Fe, indicating that changes in catchment loads, rather than changes in the efficiency of the lake as an Fe sink, was the main mechanism controlling lake water Fe concentrations. This was further supported by the fact that Fe accumulation rates in the sediment were increasing over time along with increasing Fe concentrations in the water column (Paper IV). As these conclusions are based on investigations of a single lake and with a relatively long residence time, lakes with a range of residence times should be studied. This would provide a more comprehensive understanding of how Fe concentrations and fluxes respond to altered precipitation patterns in a changing climate.

Finally, positive trends in Fe concentrations were more frequent and occurred at a higher rate in catchments with a large coniferous cover (Paper I). The drastic increase in spruce volume in the catchment of Lake Bolmen was also a significant predictor of long-term changes in Fe concentrations in the lake (Paper IV). These results suggest that land-use changes is an important factor behind Fe increases in freshwaters, potentially due to the gradual build-up of organic soil layers below aging coniferous forest that can leach accumulated Fe and DOC to hydrologically connected streams. The concurrent increases in Fe, Si and OC accumulation rates in the sediments in Lake Bolmen are in line with higher weathering rates, and export of minerals and OC, in response to the expansion of conifers in the lake catchment the past decade (Paper IV). Moreover, that Fe increases corresponded well with increases in Si in Paper I, is also in line with high weathering rates under coniferous forests as a mechanism of mobilization (Humborg et al. 2004). Hence, the previously proposed importance of afforestation in explaining temporal trends in water color (Kritzberg 2017) may also hold for Fe. Future studies should study in greater detail the role of afforestation in increased soil weathering and Fe mobilization, for instance by zooming in on soil processes and soil water chemistry under spruce stands of different ages. Since hydrological changes may affect runoff patterns, weathering rates, and redox conditions, studies could also address how increased precipitation affect Fe export from these soils. It is furthermore possible that weathering rates are enhanced in coniferous forests due

to high fungal activities, and that certain species have a higher Fe mobilizing capacity than others. Future studies should investigate the role of microbial processes in Fe mobilization from boreal soils.

In conclusion, of the potential drivers addressed in this thesis, afforestation is the most likely driver of increasing Fe concentrations, but climate change may enhance Fe mobilization from boreal soils through increased soil runoff, enhanced weathering rates, and altered redox conditions. Since rising Fe concentrations in freshwaters may have far-reaching consequences, further investigations of what mechanisms are causing Fe to increase in freshwaters are much needed. This knowledge is important in order to be able to predict future Fe concentrations, and to judge what kind of measures, if any, are needed to mitigate undesirable effects on freshwater systems.

Acknowledgements

Mitt första och största tack riktar jag till dig **Emma**. Tack för att jag fick möjlighet att järnforska med dig! För att du har pushat mig framåt när jag tvivlat på min förmåga, och för att du har hållit mig tillbaka när jag inte insett mina egna begränsningar. Tack för att du alltid backar upp och muntrar upp. Du kommer alltid vara en förebild i hur du tar dig an forskning med entusiasm, nyfikenhet och alltid med en stor dos humor!

Tack också till min biträdande handledare. **Gesa** – du är en sådan inspiration med ditt skarpa intellekt, din rakhet, och din oerhörda värme. Jag hoppas att jag får tillfälle att samarbeta mer med dig i framtiden. Tack **Per**. Det har känts tryggt att ha en kemist – och framförallt en Dylan-vän – med mig på järnresan. Jag har uppskattat Stanford-vistelserna, och de långa timmarna vid beamline 4-1, mycket. Du har lärt mig massor.

Lasse, tack för all uppmuntran och uppmaningar att ta det lugnt genom åren – det har värmt när järnstigen har känts snårig.

Tack **Håkan** för alla trevliga och givande mentorsmöten. Det har varit inspirerande att ta del av ditt skönlitterära skrivande. Kanske kan jag också skriva en bok en dag! Förutom den här då förstås.

Thanks also to **all collaborators** in different projects! Tack **Dan** för stödet i frysrummet, och för att du har introducerat mig till paleolimnologins fascinerande värld. I would also like to thank **Antti**. I learned a lot from you during our freeze core sampling in Finland. Your enthusiasm for varved sediments is truly inspiring. I am looking forward to digging into the -järvi archives again in a near future.

Thanks also to **Dimitri** for introducing me to the fungus *Jaapia ochroleuca* who went from being a fluffy layer messing up our microcosm measurements to being a fascinating, and efficient, Fe mobilizer.

Thanks **everyone at the Aquatic Ecology unit,** past and present, for contributing to a nice and inspiring working environment.

A special thanks to the **Bahamas group**. To my fellow **Fe-males Martin** and **Simon** for sharing my excitement for smelly waters and brown (!) blue holes, and for your support during the thesis writing. To **Raphael** for driving us safely around the island, and for the epic dark-and-stormy-dance. To "the shed group" **Varpu**, **Marcus**, **Yongcui,** **Alex**, and **Huan** that did not see much of the Bahamian sun, or the nice blue holes. To the excellent fisherman **Nan,** and to the "fish scarers" **Gustaf** and **Jerker.** Thanks all of you for contributing to making the Bahamas trip so memorable! Thanks also to **Kaj** and **Brian** for making the trip possible, and to **Christer**, **Lasse**, **Karin** and **Anders** for your support during application writing and field work. Lastly, a special thanks also to **The Little Frenchman** - je t'aime!

Emma J: det har inte blivit något band ännu men jag har inte gett upp drömmarna – i vår blir det barnvagnsrock!

Tack till **Christer** för goda råd och uppmuntran under min tid som doktorand på avdelningen.

Karin, tack för att du gav mig chansen att upptäcka att forskning är roligt i ditt labb, och för att du uppmuntrade mig till att söka en doktorandutbildning.

Tack **Olof R** för att du bidragit till att göra våra journal-club-träffar så givande. Jag har lärt mig en massa om järn, svavel och annat biogeokemiskt från dig.

Sylvie - thanks for your kindness and words of encouragement. And for all the French cookies!

Tack till enhetens hjältar **Marie**, **Calle**, och **Cecilia** för att ni löser alla praktiska problem. Och för ert sällskap och allt kattprat!

Lea - tack för alla träningspass och för att jag fick prova på att ha en kontorskompis ett tag.

Margarida – thanks for all your help with the thesis! I am looking forward to future fika dates with you and **Saghar**.

Tack också alla vänner från Lund - **Magdalena, Ulrica, Karin, Lisa, David, Ola, Julia, Boel, Mareike, Martin, Liz, Helene, Darren, Daniel, Isa, Marija**, och Alingsås - **Emelie, Hanna, Anna, Sara** m.fl. Ni betyder mycket!

Slutligen, tack **familjen** för att ni ger mig stöd! **Vidar**, ett oändligt tack för det fina omslaget, och för din kärlek och ditt tålamod genom doktorerandets galna berg-och-dalbana. Nu väntar en ny karusell! Tack också **bebis** för att du satt avhandlingsarbetet i perspektiv de senaste månaderna och gett mig något roligt att se fram emot efter doktorerandet.

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